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**Symposium II: Mechanochemistry in Materials Science**  
**MRS Fall Meeting, Nov. 30-Dec. 4, 2009, Boston, MA**

Stephen Craig, Duke University (financial chair)  
Matthias Scherge, Fraunhofer IWM  
Nancy Sottos, UIUC

**Symposium Objectives.** Damage-prone regions at surfaces and in polymeric and composite materials are difficult to detect and even harder to mitigate. Damage is preceded by complex spatial and temporal changes in stress state, and it is therefore desirable to utilize those changes in stress state to mechanically activate – without human intervention – chemical changes that favorably alter materials properties where and when they are needed. Desirable materials properties brought about in response to high-stress conditions include: (1) signal generation to warn of ensuing failure, (2) molecular structure modification to slow the rate of damage and extend lifetime (e.g., stress-induced crosslinking), and (3) repair of damage in early stages to avoid catastrophic failure. In addition, the stress fields associated with particular material uses might be productively channeled to create new molecular processes (chemical reactions) that are otherwise impossible.

The *vision for this symposium centered* on a set of fundamental, transportable knowledge that spans the nascent field of mechanically-adaptable polymers, surfaces, and composites. Tangible outcomes include: (1) numerical tools and software for the discovery and optimization of mechanically activated molecules (“mechanophores”), (2) fibers and films that can sense their mechanical state and loading history, and (3) polymeric composites that heal damage and adapt to their stress state. Mechanically active materials have the potential to broadly impact a number of defense-related materials needs such as nylon and other fabrics that possess built-in strain sensing capabilities, adaptable prosthetics, electronic components with extended lifetimes, and structural composites with improved performance.

**Summary and Highlights.** The Symposium was divided into sessions that focus on three core areas of mechanochemically active materials and material systems: *Mechanochemically Active Polymers* (which includes polymer composites), *Mechanochemistry in Tribology and Milling*, and *Mechanochemistry Under Extreme Conditions* (including, for example, high pressure waves). Within each session, there were a mix of invited and contributed talks that spanned from molecular and macroscopic modeling, to materials design and synthesis, to characterization and properties. A blend of practical and fundamental perspectives were featured, as indicated by the participation of an

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interdisciplinary group of presenters that comprises materials scientists, mechanical engineers, chemists, and physicists.

The first day of the Mechanochemistry began with a focus on polymers. During the morning session several trends in the fields of polyelectrolyte nanobrushes, biological mechanics as well as nanocomposites were introduced. There were also presentations on the principles and novelties of mechanophores, a subject that was further discussed in the second session. The audience was introduced to fundamental aspects of mechanochemistry and the mechanics of bonds. Mechanochemical modeling in polymers was discussed for several polymer classes (gels, copolymers etc.). Interesting talks were also given on applied systems such as thermoplastic polyurethanes and potential self-healing mechanisms.

On the second day tribological research was discussed, starting with the modeling of tribo-systems with carbon, water and amorphous silica. Experimental work was also presented, ranging from thermally controlled nanocontacts and microscopic on-line topographical investigations to engine surfaces in the presence of soot. There were presentations on the mechanochemistry in the synthesis of various materials, as well as correlations with other properties, such as conductivity. Extreme conditions in mechanochemistry were introduced and discussed in the last session, including milling, collision, shock (laser shock compression), sonar influences and spalling.

The poster session, held on the first day, comprised the work of many researchers on the above fields and gave the opportunity for open discussion. Scientists representing about ten countries were given the opportunity to exchange knowledge and ideas stemming from different backgrounds and demonstrate the latest discoveries in mechanochemistry.

**Future Direction.** The symposium highlighted the current sea change occurring in the field of mechanochemistry, fueled largely by the ability to bring increasingly molecular perspectives to old and new phenomena alike. There was an overwhelming sense that methods for probing distributions of molecular stress states in a variety of extreme environments constitute a major challenge, and that continued advances in multi-scale modeling are necessary to complement ongoing experimental advances. Much excitement in particular was expressed for the idea that mechanical strains could be used to trigger local "self-healing" behavior in polymers and polymer composites, an area in which a large number of presentations seemed to be targeting.



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## II: Mechanochemistry in Materials Science

November 30 - December 1, 2009

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\* Invited paper

SESSION II1: Mechanochemistry in Polymers I  
Chair: Stephen Craig  
Monday Morning, November 30, 2009  
Room 108 (Hynes)

8:30 AM \*II1.1

**Polyelectrolyte Brushes as a Mechanochemistry Platform.** Wilhelm Huck, University of Cambridge, Cambridge, United Kingdom.

One of the key features of living organisms is their ability to convert mechanical energy stored in chemical bonds into movement. Mechanical forces acting upon organisms can be sensed in a variety of ways and there is a significant research effort to discover how external forces influence cell activity (from distortions of the cytoskeleton to the activation of gene expression and the



synthesis of proteins). The fundamental question that is central to the work discussed here, is how mechanical energy can be used to manipulate chemical reactions and ultimately to form new bonds. In our work we described the ionization of dye molecules trapped inside polyelectrolyte brushes upon mechanical deformation of the polymer chains. Further work will focus on the growth of brushes on flexible substrates and the use of bending and stretching to manipulate chemical equilibria in polyelectrolyte brushes.

#### 9:00 AM II1.2

**Design and Discovery of Mechanophores.** Jeffrey Moore, Department of Chemistry, University of Illinois, Urbana, Illinois.

An experimental approach to discover new mechanophores will be discussed. Examples involving electrocyclic ring-openings and a possible heterolytic bond cleavage will be presented.

#### 9:30 AM II1.3

**Activation of Mechanophore-Linked Polymers.** Nancy R. Sottos<sup>1,2</sup>, Jinglei Yang<sup>2</sup>, Brett Beiermann<sup>1</sup>, Cassandra M. Kingsbury<sup>1</sup>, Douglas A. Davis<sup>3</sup>, Asha-Dee N. Celestine<sup>4</sup>, Scott R. White<sup>2,4</sup> and Jeffrey S. Moore<sup>2,3</sup>; <sup>1</sup>Materials Science and Engineering, University of Illinois, Urbana, Illinois; <sup>2</sup>Beckman Institute, University of Illinois, Urbana, Illinois; <sup>3</sup>Chemistry, University of Illinois, Urbana, Illinois; <sup>4</sup>Aerospace Engineering, University of Illinois, Urbana, Illinois.

Damage in polymeric materials is preceded by complex spatial and temporal changes in stress state. Mechanical force activates covalent bonds in the polymer, but the typical result is chain scission and ultimately failure. The goal of current research is to utilize changes in stress state to mechanically activate, without human intervention, chemical changes that favorably alter the material properties of the polymer, prior to failure. Mechanoresponsive polymeric materials are created by directly linking force-activated mechanophores into the polymer chains or by using the mechanophores as crosslinkers between polymer chains. The mechanophore motif requires efficient transfer of force to a relatively small number of specific bonds in the polymer. With the goal of better understanding the mechanism for transduction of macroscopic stress at the bulk polymer level to a mechanochemical reaction on the molecular level, we investigate the influence of chain mobility and chain alignment through changes in temperature, loading rate, and loading direction for both glassy and elastomeric polymers. We selected a mechanophore with the potential to undergo a force-induced 6- $\pi$  electrocyclic ring-opening reaction that is accompanied by a change in color and fluorescence, providing visual evidence of the local chemical reaction under mechanical deformation. Mechanochemical transduction was observed in both glassy and elastomeric polymers over a range of loading conditions. Elastomeric materials consisted of mechanophore polymerized into poly(methyl acrylate) (PMA) as either a single linked mechanophore per linear chain or as a crosslinker between chains. The effects of crosslink density and chain alignment were investigated under both tensile and shear loading conditions. Glassy materials consisted of mechanophore-linked linear poly(methyl methacrylate) (PMMA) and polystyrene (PS), as well as mechanophore crosslinked PMMA beads. We characterized the threshold stress and strain levels required to produce colour change in the active PMMA beads over a range of strain rates and temperatures. The yield stress and threshold stress both increased linearly with the natural log of the strain rate and decreased with increasing temperature, indicating that the mechanochemical reaction in the bulk polymer may be a rate process strongly affected by strain rate and temperature. Work is in progress to establish the role of chain alignment on mechanochemical activation of the linear PMMA and PS materials.

#### 9:45 AM II1.4

**Nanomechanical Sequencing of Collagen Molecules: Linking Genetics to Mechanics.** Sebastien Uzel<sup>1</sup> and Markus J. Buehler<sup>2</sup>; <sup>1</sup>Mechanical Engineering, MIT, Cambridge, Massachusetts; <sup>2</sup>Civil Engineering, MIT, Cambridge, Massachusetts.

Collagen is the most important structural protein in biology and is responsible for the strength and integrity of tissues such as bone, teeth, cartilage and tendon. Here we report a systematic computational sequencing of the effect of amino acid motif variations on the mechanical properties of single tropocollagen molecules under mechanical stress, with a particular focus on nonlinear elastic (hyperelastic) deformation at varying applied strains. By utilizing a bottom-up computational materiomics approach applied to four model sequence motifs found in human type I collagen, we show that variations in the amino acid motif severely influence the hyperelastic behavior of tropocollagen molecules, leading to softening or stiffening behavior. We also show that interpeptide interactions via H-bonds vary strongly with the type of motif, which implies that it plays a distinct role in the molecule's stability and mechanical integrity. The most important implication of our results is that deformation in tropocollagen molecules is highly inhomogeneous, since softer regions deform more than stiffer regions, potentially leading to strain and stress concentrations within collagen fibrils. We confirm the hypothesis of inhomogeneous molecular deformation through direct simulation of stretching of human type I collagen that features the physiological amino acid sequence. Through nanomechanical sequencing of a full length 300 nm long human type I collagen molecule, here we report for the first time a detailed analysis of the hyperelastic properties of physiological collagen molecules and its dependence on the amino acid sequence. Through inference analysis we elucidate key biochemical and physical parameters associated with particular sequences and sequence motifs linked to a particular nanomechanical response. This quantitative link between genetics and mechanics provides a new paradigm in biomechanics, with implications for physiological processes and disease mechanisms. Our results also provide parameters for the local stiffnesses that are implemented in an existing coarse-grained bead-spring model. Our study shows that there exist significant local structural and property variations at many relevant tissue scales, from nano to macro (amino acid, molecular, fibrillar, etc.) that can not be captured by conventional nonlocal continuum theories.

#### 10:30 AM II1.5



**Amplification of Tension in Branched Macromolecules.** Sergey Panyukov<sup>2</sup>, Sergei Sheiko<sup>1</sup> and Michael Rubinstein<sup>1</sup>;

<sup>1</sup>Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina; <sup>2</sup>P. N. Lebedev Physics Institute, Russian Academy of Sciences, Moscow, Russia.

We propose a framework for the design of branched macromolecules that are capable of building up a high tension (~nN) in their covalent bonds in solution without applying an external force. The tension is self-generated due to intramolecular interactions between branches and can be controlled by changing the solvent quality. Furthermore, this tension can be amplified from the pN to nN range by focusing lower tensions from its numerous branches to a particular section of the designed molecule. The simplest molecular architecture, which allows this tension amplification is a so-called pom-pom macromolecule composed of a relatively short linear spacer and two z-arm stars at the spacer ends. Intrinsic tension in the star arms is amplified by a factor of z and focused to the spacer. There are other types of branched macromolecules, e.g. molecular brushes that have similar focusing and amplification properties, and moreover, can transmit tension along their backbone. Adsorption of those branched molecules on a substrate results in further increase in tension as compared to molecules in solution.

**11:00 AM II1.6**

**Spiropyran Mechanophores as Probes of Mechanochemical Activation.** Douglas A. Davis<sup>1,3</sup>, Nancy R. Sottos<sup>2,3</sup>, Scott R. White<sup>4,3</sup> and Jeffrey S. Moore<sup>1,2,3</sup>; <sup>1</sup>Department of Chemistry, University of Illinois, Urbana-Champaign, Urbana, Illinois;

<sup>2</sup>Department of Materials Science and Engineering, University of Illinois, Urbana-Champaign, Urbana, Illinois; <sup>3</sup>Beckman Institute, University of Illinois, Urbana-Champaign, Urbana, Illinois; <sup>4</sup>Department of Aerospace Engineering, University of Illinois, Urbana-Champaign, Urbana, Illinois.

While the mechanochemical activation of spiropyrans within a bulk polymer has been recently demonstrated [Davis, et al. Nature 459, 68 (2009)], the effects of structural changes to the mechanophore upon the bulk mechanochemical properties have not yet been fully investigated. In order to study the interplay between the molecular and macro scales, a series of spiropyran mechanophores were synthesized in which the sites of polymer chain attachment on either side of the spiropyran were varied by shifting their positions on the two orthogonal ring systems. These variations affect the transfer of mechanical force through the cleavable spiro bond by altering the mode of bond deformation (stretching vs. twisting) or by redirecting some of the force through the spiro carbon-carbon bond (non-productive pathway). The mechanochemical properties of these new mechanophores have been studied in solution and in bulk polymers by sonication and mechanical testing, respectively.

**11:15 AM \*II1.7**

**Characterization of Mechanochemistry in Bulk and Nanocomposite Materials.** Paul V. Braun, Dara V. Gough, Corissa K. Lee, Doug A. Davis, Nancy R. Sottos, Jeffrey S. Moore and Scott R. White; University of Illinois at Urbana-Champaign, Urbana, Illinois.

Mechanochemistry, when and where did it happen? This is often the question when one studies mechanically driven chemical reactions. Any time a glassy polymer fractures, bonds are broken. However, detection of bond cleavage events is difficult given the small number of broken bonds and the generally transient nature of the product of the bond cleavage. In an engineered mechanochemically active system, the goal is generally not to simply break bonds upon fracture, but rather to drive a productive chemical reaction at some sub-critical load before a fracture event. How can such reactions be observed in bulk and nanoparticle filled polymers? Our initial studies have focused on polymers, such as polyurethane or PMMA containing the color-generating mechanophore spiropyran (SP). Application of mechanical stress to these materials results in a dramatic color change as the the spiro carbon-oxygen (C-O) bond ruptures turning the closed, colorless SP into the planar colored and highly fluorescent merocyanine (MC). SP has negligible absorption or fluorescence between 450 nm and 800 nm, while MC has an absorption peak at 577 nm and is highly fluorescent. Through confocal fluorescence microscopy, 3D spatial maps of mechanochemical activation in a compressed PMMA bead were obtained and compared to a model of the stress state within the sample. We are also using optical probes to quantify mechanochemistry in nanoparticle filled polymers where the mechanophore is covalently linked between the nanoparticle reinforcement and matrix phase.

**11:45 AM II1.8**

**Pulling Bonds Apart: Understanding the Coupling Between Force and Reactivity.** Roman Boulatov and Zhen Huang; University of Illinois, Urbana, Illinois.

The presentation will expand on our recent cover article in Nature Nanotechnology (May 2009). Dramatic changes in rates of localized reactions when a polymer is stretched underlie phenomena as diverse as operation of motor proteins, fragmentation of polymers in shear flows, at interfaces and during crack propagation, operation of actuating materials and mechanosensing. Both atomistic understanding of these phenomena and rational design of new stimuli-responsive and other "smart" polymers requires quantitative framework within which to discuss such rate changes. Whereas the effect of molecular strain on reactivity of small molecules is often captured by strain energy, changes in the kinetics of localized reactions in stretched polymers do not correlate with the total strain energy of the polymer. The breakdown arises from the extensive property of strain energy. In contrast, strain energy gradient - molecular restoring force - is a size-invariant measure of molecular strain. As such it is, at least in theory, applicable to a reactant of any size - from an isolated functional group to macromolecular assemblies. However, how to integrate force into modern kinetic theories is not known. Localized covalent chemistries comprise conceptually the most tractable systems to develop new and test the existing models relating force and rate (so-called chemomechanical model). Yet these reactions are particularly difficult to study systematically using conventional force spectroscopy. I will describe the molecular design and chemical realization of a molecular force probe that acts as a functional substitute of a microscopic force probe (such as an AFM



tip) at the natural scale of a covalent bond. Using this molecular force probe we have demonstrated experimentally that the simplest chemomechanical kinetic model is remarkably robust in case of single-barrier reactions, but breaks down even in the simplest case of a corrugated energy landscape (pre-exponential kinetics). The robustness of the single-coordinate chemomechanical model opens up possibilities of rationally designing "mechanophores" - monomers, whose incorporation in polymers endows them with stimuli-responsive properties.

#### SESSION II2: Mechanochemistry in Polymers II

Chair: Nancy Sottos

Monday Afternoon, November 30, 2009

Room 108 (Hynes)

##### 1:30 PM II2.1

**Mechanochemistry From First Principles.** Mitchell Ong<sup>1,2</sup>, Lee Cremer<sup>1,2</sup> and Todd J. Martinez<sup>1</sup>; <sup>1</sup>Chemistry, Stanford University, Stanford, California; <sup>2</sup>Chemistry, University of Illinois, Urbana, Illinois.

We incorporate external force in first-principles molecular dynamics simulations, where the internal forces between atoms are determined by direct solution of the electronic Schrödinger equation. Bond cleavage and rearrangement can be realistically modelled in this framework without any preconceptions, i.e. any of the molecular bonds are free to break upon application of external force. We apply the method to two mechanophoric moieties which have been of recent experimental interest - cyclobutenes and spiropyran. We also introduce a force-modified potential energy surface (FM-PES) and show that one can optimize reaction pathways on this FM-PES. Not only barrier heights but also reaction mechanisms are shown to be influenced by the application of external force. Finally, we show the first results aimed at designing mechanophoric systems using first-principles molecular dynamics and reaction path optimization on the FM-PES.

##### 2:00 PM II2.2

**Mechanochemical Remodeling of Polybutadiene Copolymers Under Mechanical Stress.** Jeremy M. Lenhardt, Ashley L. Black and Stephen L. Craig; Chemistry, Duke University, Durham, North Carolina.

There is rapidly escalating interest in the synthesis and characterization of latent reagents and catalysts that undergo mechanically initiated activation when coupled to a directional restoring force. The construction and characterization of novel mechanophores advances the fundamental understanding of how mechanical force directs chemical reactivity, and provides access to new stress-responsive materials; for example polymers that strengthen or repair autonomously at the molecular level. Seminal work on benzocyclobutene (BCB) and spiropyran moieties incorporated near the center of polymers has shown that mechanical force can be used to efficiently direct ring-open chemistry. These studies demonstrate important steps toward in situ mechanochemistry for stress-responsive polymers. We have designed and quantified the activity of gem-dihalocyclopropane (gDHC) copolymers derived from poly(butadiene). When subjected to ultrasonication, the mechanical copolymer response differs depending on the type of gem-dihalogen (F, Cl, Br). The reactivity is not observed in low molecular weight copolymers nor in side chain copolymers, consistent with mechanically induced reactivity due to the elongational strain of the polymers in the sonication flow fields. The ring openings occur several hundred times more frequently than polymer chain scission, and cis-coupled gem-dichlorocyclopropanes are slightly more reactive than their trans isomers. The ability to dramatically and specifically alter the structure of the polymer backbone through a coupled restoring force suggests new routes to post-synthetic polymer modification and motivates the design of easily scalable mechanophores for applications in stress-responsive polymers.

##### 2:15 PM II2.3

**N-Heterocyclic Carbenes: Applications In Mechanically-Activated Reactions and Self-Healing Materials.** Christopher Bielawski, Chemistry & Biochemistry, University of Texas at Austin, Austin, Texas.

It has been recently reported that chemical transformations can be facilitated or even biased through the application of mechanical forces.<sup>1,2</sup> Building upon this concept, we seek to develop systems whereby mechanochemical transduction can be used to facilitate stoichiometric coupling reactions and to "turn on" catalytic reactions, particularly as a means to facilitate repair in damaged polymeric materials. Emphasis in our group has been directed toward the use of appropriately derivatized N-heterocyclic carbenes (NHCs) and their complexes with various transition metals and organic electrophiles. Since the formation of such complexes is known<sup>3</sup> to be reversible, our hypothesis is that the application of mechanical forces may liberate free NHCs and/or catalytically-active transition metal complexes, either of which may be used to facilitate polymerization reactions (stoichiometrically or catalytically). This presentation will describe our efforts toward the development of systems that facilitate various coupling reactions as well as the ring-opening polymerization of strained carbo- and heterocycles will be described. The potential of using these systems as the basis for self-healing materials will also be discussed.

##### 2:45 PM II2.4

**Mechanochemistry In Thermoplastic Polyurethanes.** Corissa Lee<sup>1,3</sup>, Douglas Davis<sup>2,3</sup>, Jeffrey S. Moore<sup>1,2,3</sup>, Nancy R. Sottos<sup>1,3</sup> and Paul V. Braun<sup>1,2,3</sup>; <sup>1</sup>Materials Science and Engineering, University of Illinois at Urbana Champaign, Urbana, Illinois; <sup>2</sup>Department of Chemistry, University of Illinois at Urbana Champaign, Urbana, Illinois; <sup>3</sup>Beckman Institute, University of Illinois at Urbana Champaign, Urbana, Illinois.

Thermoplastic polyurethane (TPU) containing the color-generating mechanophore spiropyran (SP) was synthesized and



characterized. Polyurethane was chosen because it is a step growth engineering polymer, which enables incorporation of defined mole fractions of SP in a high performance engineering material. The TPU consisted of either all soft segment (polytetramethyleneglycol) or a mixture of a soft and hard segment (1,4 butanediol) monomers. In both cases, the SP mechanophore was exclusively covalently attached to the soft segment of the TPU. Application of mechanical stress resulted in a dramatic color change as the the spiro carbon-oxygen (C-O) bond ruptures turning the closed, colorless SP into the planar highly colored and highly fluorescent merocyanine (MC) group. The appearance of bright purple color after the sample is stretched is a manifestation of this stress-induced transition from spiropyran (SP) to merocyanine (MC). Using UV-Vis spectroscopy the relationship between the absorption and the mechanical stress was quantified. SP has negligible absorption between 450 nm and 800 nm, while MC has an absorption peak at 577 nm. Fluorescence images taken as a load was applied to the polymer show as expected an increase in fluorescence with increasing stress, further confirming the stress-induced transition from SP to MC. Once the SP mechanophore has been converted to the MC form by the applied load, over time the color fades as the MC closes and converts back to the SP conformation. Fluorescence microscopy was used to quantify the rate at which MC reverses back to SP in soft segment TPU. After the mechanophore was activated the sample was left to decay in the dark. Fluorescence images of the activated MC reversing back to SP were collected and fitted to a single exponential decay equation with a time constant of about 30 minutes. Recently, we have begun to explore the addition of silica nanoparticles to this composite. Silica nanoparticles, which serve as a reinforcement phase in the TPU, were surface functionalized with spiropyran molecules. The functionalized nanoparticles were dispersed and then covalently attached into the polyurethane matrix phase, placing the mechanophore at the interface between the reinforcement and matrix phase. Mechanochemical activation studies of this composite system are ongoing.

### 3:30 PM \*II2.5

**Molecular Tensile Machines.** Sergei S. Sheiko<sup>1</sup>, Natalia Lebedeva<sup>1</sup>, Insun Park<sup>1</sup>, Krzysztof Matyjaszewski<sup>2</sup>, Alper Nese<sup>2</sup>, Michael Rubinstein<sup>1</sup> and David Shirvanyants<sup>1</sup>; <sup>1</sup>Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina; <sup>2</sup>Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania.

Mechanical activation of chemical bonds plays a vital role in biology, chemistry, and materials engineering. Usually, one should use an external tool to induce deformation of bond length and bond angles. Recently, we have discovered a class of macromolecules that self-generate tension in their covalent bonds without applying any external force. One example is molecular bottle-brushes, highly branched macromolecules with side chains densely grafted to a long polymer backbone. These polymer architectures are regarded as molecular tensile testing machines, wherein the brush section generates force and transmits it to covalent bonds in the backbone. The bond tension depends on molecular architecture and interaction of macromolecules with the surrounding environment. Through variation of temperature, solvent, and substrate composition, one can control bond tension in a broad range from pico- to nano-Newtons, which is sufficient to break both weak H-bonds and strong covalent bonds. Even when the bonds are not broken, such tremendous tension has profound effect on the electronic structure, which directly impacts molecular reactivity, optical properties, and conductivity. We will elucidate physical mechanisms that generate tension within branched macromolecules at interfaces and discuss the effect of the tension on the molecular reactivity and electronic properties. We will also show how the smart molecular design allows fine tuning of the tension distribution and enable mechanical activation of chemical reactions at specific chemical bonds within specific macromolecules. The bond tension is accurately controlled by the length of the side chains, the surface energy of the substrate, and temperature. Systematic variation of these parameters enables quantitative analysis of the bond potential and the corresponding rate constants.

### 4:00 PM \*II2.6

**Correlations Between Structural Developments and the Mechanical Response of Reacting Chemical Systems.** Michael Aldridge<sup>1</sup>, John Kieffer<sup>1</sup>, Chandrashekar Shankar<sup>1</sup>, Changhua Zhen<sup>1</sup>, Mary Caruso<sup>2</sup> and Jeffrey Moore<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; <sup>2</sup>Chemistry, University of Illinois, Urbana, Illinois.

We have studied the cure kinetics of cross-linking polymers using a combination of concurrent in-situ Raman and Brillouin light scattering and molecular-scale simulations. Raman light scattering allows us to track the progress of chemical changes in the system induced by polymerization. It can furthermore be used to quantify the local strains that affect individual bonds in the structure. At the same time Brillouin scattering allows us to monitor the changes in the polymer's elastic properties directly during the curing process, revealing information about the degree of connectivity and structural integrity of the network. To interpret experimental findings, we first use reactive molecular dynamics simulations to generate realistic models of the network structures that form. The mechanical properties of these simulated structures can be directly calculated. Furthermore, using DFT methods we calculate the Raman active spectral bands associated with the various bonding configurations that occur in these structures, and by scaling the band intensities according to the structural features' concentrations, we determine simulated Raman spectra for comparison with the experimental data. This combination of experiments and simulations allows us to establish the relationship between the current reactive state of molecular configurations and their mechanical properties as a function of the degree of cure. We illustrate this approach for dicyclopentadiene (DCPD), which is used as a remedial agent in self-healing materials, as well as for epoxy which has widespread use in polymer-matrix composites.

### 4:30 PM \*II2.7

**Modelling Mechano-chemical Transduction In Responsive Polymer Gels.** Anna Balazs, Olga Kuksenok and Victor Yashin; University of Pittsburgh, Pittsburgh, Pennsylvania.

A vital function performed by skin is to send a chemical alarm signal throughout the system in response to irritation or damage. Using our 3D model for chemo-responsive gels, we design a coating that can perform an analogous, biomimetic function. Our



system consists of a polymer gel undergoing the Belousov-Zhabotinsky (BZ) reaction. We show that such coatings respond to a spatially localized mechanical force by exhibiting a range of signaling behavior. For example, an initially stationary gel can emit transient waves in response to a sufficiently weak, localized impact. A stronger localized impact, however, can generate a global signal, which encompasses both chemical waves and surface ripples that propagate across the entire sample. This complex dynamical response persists even after the force is lifted. Furthermore, the spatial patterns formed by these oscillating gels reveal the location and magnitude of the applied force. Our findings open up the possibility of harnessing BZ gels for a range of applications, such as creating sensors that transmit a global signal in response to a local mechanical impact.

SESSION II3: Poster Session: Mechanochemistry  
Chairs: Stephen Craig, Matthias Scherge and Nancy Sottos  
Monday Evening, November 30, 2009  
8:00 PM  
Exhibit Hall D (Hynes)

### II3.1

**Crevice Corrosion and Cracking Behavior of Cold Rolled Type 304 Stainless Steel In Chloride Environment.** Shunji Kajikawa<sup>1,2</sup>, Yasuaki Isobe<sup>1</sup> and Masazumi Okido<sup>2</sup>; <sup>1</sup>Materials R and D, Denso Cooperation, Kariya, Aichi, Japan; <sup>2</sup>Materials Science and Engineering, Nagoya University, Nagoya, Aichi, Japan.

The salt damage such as the snow melting salts in winter or the sea salt particle flying in the coast region has significant effect on the corrosive environment of the automobile. Moreover, the corrosive environment of the automobile become more severe by the wet/dry cyclic condition, for example, a car gets wet with the splash water and dryness by the thermal loading while driving. On the other hand, the further application of the high strength stainless steel to the automobile parts is expected because it can contribute durability and lightening. Then, it is important to clarify the corrosion characteristic of this material under the salt damage environment. In this study cold rolled type304 stainless steel pipe with shot peening were used to investigate the corrosion property of high strength type304 stainless steel for automotive applications in a salt damage environment. The hardness of the pipe was about HV450, and a clear difference was not admitted in the thickness direction. A crevice was created between the outside of the pipe and an O-ring, and the pipe was applied stress by press fitting of another part. The corrosion property of the sample was evaluated in an automotive field test in Okinawa. Cracking from a corrosion pit was observed in the crevice. The Electron Probe Micro Analysis(EPMA) indicated that pitting corrosion was caused by chloride (from sea salt) concentrated in the crevice. The crack occurred in the residual compressive stress layer created by shot peening. In this regard, it was confirmed by the XRD analysis that about 85% of the metallographic structure had been transformed into the martensite. And the observation of the metallographic structure by the Electron Back Scatter Diffraction(EBSD) clarified the crystal grain was greatly transformed by the strong processing. It means that the accumulation of strain occurred. These two factors are considered to raise the receptivity to the crack generation of this sample. A crack generated at a corrosion pit was reproduced in a wet/dry cyclic corrosion test after one flash of artificial seawater. To investigate the crack generating mechanism, a corrosion pit was previously generated on the sample by cyclic corrosion test, after which a cathodic charge test in artificial sea water was done. Similar cracking from a corrosion pit was observed on the sample after this test. Therefore, the cracking is presumed to be Hydrogen Embrittlement-Stress Corrosion Cracking(HE-SCC)

### II3.2

**Estimate of Hydrogen Density at Starting Point for Crevice Corrosion and Cracking of Cold Rolled Type 304 Stainless Steel.** Shunji Kajikawa<sup>1,2</sup>, Yasuaki Isobe<sup>1</sup>, Akio Kuromiya<sup>1</sup> and Masazumi Okido<sup>2</sup>; <sup>1</sup>Materials R and D, Denso Cooperation, Kariya, Aichi, Japan; <sup>2</sup>Materials Science and Engineering, Nagoya University, Nagoya, Aichi, Japan.

In the past work of authors, a cold rolled type304 stainless steel pipe with shot peening was prepared. A crevice was created between the outside of the pipe and an O-ring, and the pipe was applied stress by press fitting another part. Cracking from a crevice corrosion pit was observed in a chloride environment, and it was presumed to be Hydrogen Embrittlement-Stress Corrosion Cracking(HE-SCC). Provided that the crack is caused by HE-SCC, it is thought that hydrogen is generated by corrosion reaction and the SUS304 pipe absorbs it more than its critical level. Generally, the hydrogen distribution in the steel is analyzed in the condition that the hydrogen concentration of the environment is constant as the high-pressure hydrogen gas environment etc. In the case of HE-SCC described above, however, the hydrogen concentration is presumed to change with pitting growth, and there is no example of analysis in such condition. In this work, cyclic corrosion tests were conducted using the samples with no press-fitting part. The hydrogen density at the initiation point of crevice corrosion and cracking was estimated by following technique. First, the amount of hydrogen diffused from the corrosion pit was measured using Thermal Desorption Spectroscopy (TDS), and the number of pits was measured. Then, the average hydrogen quantity in a pit was derived. On the other hand, it is thought that hydrogen is generated by the hydrolysis of a metallic salt and the cathode reaction of the hydrogen ion in the pit. Therefore, the amount of the hydrogen is proportional to the quantity of corrosion amount. Then, assuming that pitting corrosion takes the form of half sphere shape and grows with time, the simulation model was made that the hydrogen absorbed and diffused from the pit surface with the development of corrosion. The profile of the hydrogen density in SUS304 from pit initiation till crack initiation was calculated based on this model. The calculated profile of the hydrogen density was compared with the amount of hydrogen measured by cyclic corrosion test. As a result, the hydrogen concentration at the crack starting point was derived 0.3ppm. At this density level, He-SCC can occur in high strength SUS304.

### II3.3

**Mechanically-Induced Solvent Based Self-Healing.** Mary M. Caruso<sup>1,7</sup>, Benjamin J. Blaiszik<sup>2,7</sup>, Gerald O. Wilson<sup>3</sup>, Christian L.



Mangun<sup>4</sup>, Nancy R. Sottos<sup>5,7</sup>, Scott R. White<sup>6,7</sup> and Jeffrey S. Moore<sup>1,5,7</sup>; <sup>1</sup>Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>2</sup>Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>3</sup>Autonomic Materials Incorporated, Champaign, Illinois; <sup>4</sup>CUAerospace, Champaign, Illinois; <sup>5</sup>Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>6</sup>Aerospace Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>7</sup>Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Mechanical damage to bulk polymers typically begins as a microcrack which can lead to eventual failure of the material if there is no process to inhibit crack growth. In living materials, this damage initiates a healing response. Following the example of nature, self-healing polymers are engineered with the unique ability to extend the lifetime of materials by preventing crack propagation using various chemical mechanisms that are triggered by crack formation. Many chemical reactions require the use of a solvent. Liquid-filled microcapsules have been prepared with various core components and are embedded within a bulk polymer during processing. By compartmentalizing reactive fluids containing a solvent into a bulk material, in situ reactions occur upon damage in the form of a crack. A crack propagating through the bulk material ruptures the embedded microcapsules, thus releasing solvent-based mixtures into the crack plane of the sample. Solvent-based self-healing reactions that occur within epoxies, thermoplastics, and bone cement materials will be presented in detail.

#### II.3.4

**Effect of H<sub>2</sub>O<sub>2</sub> in Alkaline Slurry on Polishing Rate of Crystalline Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> Film in Chemical Mechanical Planarization.** J. Y. Cho<sup>1,2</sup>, J. H. Park<sup>1</sup>, U. Paik<sup>3</sup>, C. H. Ryu<sup>4</sup> and J. G. Park<sup>1,2</sup>; <sup>1</sup>Advanced Semiconductor Material and Device Development Center, Hanyang university, Seoul, Korea, South; <sup>2</sup>Department of Nanoscale Semiconductor Engineering, Hanyang university, Seoul, Korea, South; <sup>3</sup>Division of Advanced Materials Science Engineering, Hanyang university, Seoul, Korea, South; <sup>4</sup>Research & Development Division, Hanyang university, Icheon, Kyongki-do, Korea, South.

In the chemical mechanical planarization (CMP) process of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST), the polishing rate selectivity of GST to a surrounding dielectric (SiO<sub>2</sub>) is an important factor not only to obtain sharp interface between GST and top electrode, but also to increase the mass production of PRAM devices. This work focused on understanding the effect of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidizer on the polishing rate of crystalline GST film during CMP. GST and SiO<sub>2</sub> wafers were polished, respectively, to determine the polishing rate and polishing selectivity of them in alkaline slurry with various H<sub>2</sub>O<sub>2</sub> concentrations from 0 to 3 wt%. It was observed that GST polishing rate was sharply increased at the low concentrations of H<sub>2</sub>O<sub>2</sub>, less than 0.5 wt% H<sub>2</sub>O<sub>2</sub>, and then saturated or slightly increased with the further addition. However, SiO<sub>2</sub> polishing rate was only slightly increased with a concentration of H<sub>2</sub>O<sub>2</sub>. As a result, polishing selectivity of GST to SiO<sub>2</sub> showed over 100:1 at 0.4 wt% H<sub>2</sub>O<sub>2</sub>. To understand the effect of H<sub>2</sub>O<sub>2</sub> on GST, potentiodynamic polarization test and X-ray photoelectron spectroscopy (XPS) measurement were carried out. In potentiodynamic polarization test, the corrosion current density at low H<sub>2</sub>O<sub>2</sub> concentrations is greatly increased, which almost corresponds to that of GST polishing rate. In addition, in XPS spectra of GST, the peaks of Ge-oxide and Sb-oxide bonds increased with H<sub>2</sub>O<sub>2</sub> concentration, which almost coincided with the increasing trend of corrosion potentials in the potentiodynamic polarization test. It is thought that, during polishing, GST-oxides were formed on the surface, and then simultaneously removed by mechanical abrasion. Therefore, it is deduced that, when the slurry contains low concentrations of H<sub>2</sub>O<sub>2</sub>, the chemical action is more dominant than mechanical action in high polishing rate of GST. Consequently, the concentration of H<sub>2</sub>O<sub>2</sub> is a critical factor in GST CMP slurry. In particular, we suggest that, in order to high polishing selectivity of GST to SiO<sub>2</sub>, concentration of H<sub>2</sub>O<sub>2</sub> less than 1 wt% in alkaline slurry is more preferable than that of higher concentrations. Acknowledgement \* This work was financially supported by the Acceleration Research Program of the Korea Science and Engineering Foundation and the Brain Korea 21 Project in 2009. We thank Sumco Corp. and Hynix Semiconductor Inc. for helping us with our experiments.

#### II.3.5

**Mechanistic Insights into Shear-Induced Polymer Mechanochemistry.** Ashley L. Black, Jeremy M. Lenhardt and Stephen L. Craig; Chemistry, Duke University, Durham, North Carolina.

Acoustic cavitation provides a means of mechanically activating reagents by coupling them to a shear-induced directional restoring force. The synthesis and characterization of these highly reactive species is an area of high interest. A series of geminal dihalocyclopropane polybutadiene derivatives have been synthesized and used as a probe to investigate the mechanism of sonochemical, shear-induced polymer mechanochemistry. The effects of concentration, chain entanglement, molecular weight, solvent, and mechanophore stereo- and regiochemistry on polymer mechanochemistry have been systematically studied. The results and their implications for mechanophore design in bulk polymers will be discussed.

#### II.3.6

**Mechanically Induced Color Change and Fluorescence in Mechanophore-Linked Glassy Polymers.** Brett Beiermann<sup>1,2</sup>, Jillian Franke<sup>1</sup>, Asha Dee Celestine<sup>2,3</sup>, Douglas Davis<sup>2,4</sup>, Jinglei Yang<sup>2</sup>, Jeff Moore<sup>2,4</sup>, Scott White<sup>2,3</sup> and Nancy Sottos<sup>1,2</sup>; <sup>1</sup>Materials Science And Engineering, University of Illinois, Urbana, Illinois; <sup>2</sup>Beckman Institute, University of Illinois, Urbana, Illinois; <sup>3</sup>Aerospace Engineering, University of Illinois, Urbana, Illinois; <sup>4</sup>Chemistry, University of Illinois, Urbana, Illinois.

Mechanoresponsive functionality is imparted to glassy poly(methyl methacrylate) (PMMA) and polystyrene (PS) through a molecular based strategy, whereby force-activated mechanophores serve as cross-links between or are linked directly into polymer chains. In this study, we incorporate a color-generating mechanophore that undergoes a force-induced 6- $\pi$  electrocyclic ring-opening reaction [1]. This well characterized molecule reversibly transforms from a closed, colorless spiropyran (SP) to a



highly colored, planar merocyanine (MC) structure by rupture of the spiro carbon-oxygen bond. The increased conjugation of the MC form shifts the absorption to longer wavelengths, giving rise to visible color and fluorescence. We investigate two different routes to incorporate the SP mechanophore in glassy polymers. In the first method, SP serves as a cross-linker suspension copolymerized with MMA to produce PMMA beads of diameter 100-500  $\mu\text{m}$ . Because the cross-linked beads cannot be molded into a suitable specimen geometry, they are tested in a diametral compression set-up. Color changes, with a peak at 560 nm, and fluorescence are observed to emerge from the center of the beads at strain levels just above their yield point. In the second method, the SP mechanophore serves as the initiator for atom transfer living radical polymerization (ATRP) and is linked directly into the chain. The linear PMMA and PS formed by this reaction were hot pressed into samples suitable for mechanical loading. Ring opening reactions driven by UV light showed color change with absorption peaks at 570 nm and 610 nm for SP-linked PMMA and PS, respectively. In preliminary mechanical experiments, ATRP synthesized PMMA has also indicated fluorescence and color change after damage in thin films. Testing is in progress to assess the role of chain alignment and chain mobility on mechanoactivation. Future work also includes characterization of SP-linked PS. [1] Potisek, S.L., Davis, D.A., Sottos, N.R., White, S.R., Moore, J.S. 2007, Mechanophore-Linked Addition Polymers. *J. Am. Chem. Soc.* 129, 13808-13809.

### II3.7

**Mechanically Triggered Binding and Release of Metal Ions.** Austin N. Pickett<sup>1</sup> and Paul V. Braun<sup>1,2,3</sup>; <sup>1</sup>Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>2</sup>Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>3</sup>Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Over the past few years, considerable strides have been made in the field of autonomic materials including materials which self-heal through the mechanically triggered release of encapsulated healing agents (1) and the mechanically activated cleavage of specific bonds in a polymer backbone (2). We now are demonstrating the mechanically triggered binding and release of metal ions through the use of mechanochemistry. For example, removal (binding) of an ion is accomplished with a spiropyran mechanophore incorporated into a polymer chain. Upon application of mechanical stress, this molecule goes from a neutral, non-chelating form to a polar, chelating form. The metal ion then binds to the molecule. Such metal binding could be utilized, for example, to activate a metal ion-inhibited catalyst. Work thus far has been performed for calcium ion binding, and the study of more inhibition-specific ions is ongoing. Following a similar procedure, except with a different mechanophore, the mechanically triggered release of ions is also ongoing. (1) S.R.White, N.R. Sottos, J. Moore, P. Geubelle, M. Kessler, E. Brown, S. Suresh, and S. Viswanathan: Autonomic healing of polymer composites. *Nature*, 409, 794 (2001). (2) D.A. Davis, A. Hamilton, Y. Yang, L.D. Cremer, D.V. Gough, S.L. Potisek, M.T. Ong, P.V. Braun, T.J. Martinez, S.R. White, J.S. Moore and N.R. Sottos: Force-induced activation of covalent bonds in mechanoresponsive polymeric materials. *Nature*, 459, 68 (2009).

### II3.8

**Tensile and Shear Activation of Mechanophore Linked Elastomeric Polymers.** C. M. Kingsbury<sup>1,5</sup>, A. R. Hamilton<sup>2,5</sup>, D. A. Davis<sup>3,5</sup>, S. R. White<sup>4,5</sup>, J. S. Moore<sup>3,5</sup> and N. R. Sottos<sup>1,5</sup>; <sup>1</sup>Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>2</sup>Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>3</sup>Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>4</sup>Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>5</sup>Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, Illinois.

A new strategy is employed to impart productive mechanochemical response to an elastomeric polymer. Force sensitive molecules, termed mechanophores, are successfully linked in poly (methyl acrylate) (PMA) through a SET-LRP reaction [1,2]. Evidence of local chemical reaction is provided by a color generating spiropyran (SP) mechanophore that undergoes an electrocyclic ring opening reaction under mechanical deformation. Here we investigate the role of tensile and shear loading on bulk polymer specimens. Mechanophore linked PMA-SP-PMA was produced at a molecular weight of 65 kDa and was then molded using a hot press into the desired specimen geometry. Cyclic tensile loading caused the mechanochromic PMA to change from a clear/yellow color to a vivid red color. Color change was quantified through RGB analysis of digital images acquired during testing. A red color emerges in the specimen as a function of increasing plastic strain. Shear testing was also performed on the mechanophore linked PMA in linear and crosslinked forms. The linear polymer (PMA-SP-PMA) was molded into rectangular bars (2 mm x 0.5 mm x 25 mm) and the crosslinked polymer (xPMA-SP) was molded into cylindrical bars of varying length (4.25 mm dia.). Both specimens were tested using a torsion test fixture and a TA Instruments AR-G2 rheometer. The linear PMA-SP-PMA was tested in a dynamic torque controlled test at room temperature. This test allowed the sample to undergo large strains in torsion without failure and produced interesting color patterns. Crosslinked xPMA-SP (0.09% crosslink density) was tested in both dynamic and static torque controlled tests at 5° C and 15° C. Room temperature static torque controlled tests were also performed on crosslinked xPMA-SP with crosslink densities of 1% and 2%. These cylindrical samples showed color change just before failure at shear strains over 200%. Experiments are in progress to understand the role of crosslink density, temperature, and plastic deformation on the shear-induced color change. [1] Potisek, S.L., Davis, D.A., Sottos, N.R., White, N.R., White, S.R., Moore, J.S. 2007, Mechanophore-Linked Addition Polymers. *J. Am. Chem. Soc.* 129, 13808-13809. [2] Davis, D.A., Hamilton, A., Yang, Y. Cremer, L.D., Gough, D.V., Potisek, S.L., Ong, M.T. Braun, P.V., Martinez, T.J., White, S.R., Moore, J.S., Sottos, N.R. 2009, Force-Induced Activation of Covalent Bonds in Mechanoresponsive Polymers. *Nature*. 459, 68-72.

### II3.9

**Fracture Behavior of Mechanophore-linked Glassy Polymers.** Asha-Dee Celestine<sup>1,4</sup>, Brett Beiermann<sup>2,4</sup>, Douglas Davis<sup>3,4</sup>, Jeffrey Moore<sup>3,4</sup>, Nancy Sottos<sup>2,4</sup> and Scott White<sup>1,4</sup>; <sup>1</sup>Aerospace Engineering, University of Illinois at Urbana-Champaign,



Urbana, Illinois; <sup>2</sup>Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>3</sup>Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>4</sup>Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Mechanophores (force-activated molecules) have been successfully incorporated into glassy polymers enabling a new class of mechanoresponsive polymers. In these materials mechanical energy regulates and activates the mechanophore molecule via a mechanochemical reaction [1, 2]. Applications for mechanochemical polymers include monitoring and assessing damage and initiating self-healing reactions. In this study we explore the mechanical behavior of poly (methyl methacrylate) (PMMA), a glassy polymer, which contains the mechanophore spiropyran (SP). Spiropyran is a molecule which undergoes an electrocyclic ring-opening reaction under tensile deformation. The rupture of the spiro carbon-oxygen bond is accompanied by a vivid color change from yellow to blue. Linear SP-PMMA is synthesized using the ATRP method where the PMMA is attached to position 5' of the indole side and position 8 of the benzopyran side of the SP mechanophore. This ensures that the spiro carbon-oxygen bond is preferentially stressed. Mechanical test samples are obtained by compression molding this material at temperatures just above the glass transition temperature. Material properties such as storage and loss moduli and tan delta are determined through Dynamic Mechanical Analysis (DMA). The fracture behavior of the mechanophore-linked polymer is also examined through the Double Cleavage Drilled Compression (DCDC) test method. From these tests, the fracture toughness of the SP-PMMA and the stress required to activate SP at the crack tip are ascertained. Environmental stability for SP activation and reversal are carried out through testing over a range of temperature, applied stress, loading rate, and UV exposure. These results are then compared to those of control samples in which the mechanophore (SP) is absent, or tethered in positions in which no mechanochemical activation is expected. [1] Davis, D.A., Hamilton, A., Yang, Y., Cremer, L.D., Gough, D.V., Potisek, S.L., Ong, M.T., Braun, P.V., Martinez, T.J., White, S.R., Moore, J.S. and Sottos, N.R. 2009, Force-Induced Activation of Covalent Bonds in Mechanoresponsive Polymeric Materials. *Nature*. 459, 68-72. [2] Potisek, S.L., Davis, D.A., Sottos, N.R., White, N.R., White, S.R., Moore, J.S. 2007, Mechanophore-Linked Addition Polymers. *J. Am. Chem. Soc.* 129, 13808-13809.

### II3.10

**Mechano-Chemical Processing of Multinary Complex Hydrides for Reversible Hydrogen Storage.** Sesha S. Srinivasan<sup>1</sup>, Michael Niemann<sup>1</sup>, Jason Hattrick-Simpers<sup>2</sup>, Leonid Bendersky<sup>2</sup>, Kimberly McGrath<sup>3</sup>, Yogi Goswami<sup>1</sup> and Elias Stefanakos<sup>1</sup>; <sup>1</sup>Clean Energy Research Center, University of South Florida, Tampa, Florida; <sup>2</sup>Materials Science and Engineering Lab, National Institute of Standards and Technology, Gaithersburg, Maryland; <sup>3</sup>QuantumSphere Inc., Santa Ana, California.

Multinary complex hydrides comprised of borohydrides, amides and metal hydrides have been synthesized using a solid state mechano-chemical process employing high energy ball milling. One of such systems, Li-Mg-B-N-H, exhibits potential reversible hydrogen storage behavior (>6 wt.%) at temperatures of 125-175°C. Nanocrystallization induced destabilization in the milling process is considered to be the triggering factor to obtain cycling reversibility and overall temperature reduction in hydrogen decomposition from these multinary complex structures. Structural, microstructural, and chemical characterizations were explored by metrological tools to support this dehydrogenation and reversible rehydrogenation behavior.

### II3.11

**Effect of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> Phase Property on Chemical Mechanical Polishing Performance.** H. Cui<sup>1,2</sup>, J. H. Park<sup>1</sup>, U. Paik<sup>3</sup>, C. H. Ryu<sup>4</sup> and J. G. Park<sup>1,2</sup>; <sup>1</sup>Advanced Semiconductor Materials and Devices Development Center, Hanyang University, Seoul, Korea, South; <sup>2</sup>Department of Electronics and Communications Engineering, Hanyang University, Seoul, Korea, South; <sup>3</sup>Advanced Materials Science Engineering, Hanyang University, Seoul, Korea, South; <sup>4</sup>Research and Development Division, Hynix Semiconductor Inc, Icheon, Kyongki-do, Korea, South.

Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST) has been used as the phase change material in the Chalcogenide Random Access Memory for its easy amorphization process and short crystallization time. In recent years, the confined structure is commonly used to reduce the reset current. In this structure, chemical mechanical planarization (CMP) is applied to remove the overburdened GST material and obtain a defect-less surface after gap filling. Here, the deposited GST can be either the crystalline or amorphous, depending on its deposition conditions. Thus, it is necessary to investigate comparatively the CMP characteristics of both amorphous and crystalline GST. The CMP characteristics of amorphous and crystalline GST were investigated in an alkaline slurry in which Tetramethyl Ammonium Hydroxide (TMAH) was used as the pH titrant. Our previous work has demonstrated that TMAH can effectively remove the native oxides on the surface of amorphous GST, and facilitate the material removal rate. In this work, it was found that in the presence of TMAH 0.12 wt%, the amorphous GST shows a considerably larger polishing rate than the crystalline GST. It was confirmed that the hardness difference between the two phases is not the main factor that determines the polishing rate. Surprisingly, a more reactive corrosion nature of the crystalline GST in the slurry was found by the corrosion behavior. The surface characteristics of amorphous and crystalline GST after dipping in the slurry were analyzed by the X-ray Photoelectron Spectroscopy. A strong decrease in the Te 3d metal peaks in the amorphous GST was observed, which illustrates that a selective corrosion of Te element in the amorphous GST occurs. This selective corrosion of Te elements in the amorphous phase is probably resulted from the different local bonding structure between the amorphous and crystalline GST. After a substantial dissolution of Te, it may lead to the change or collapse of local bonding structure, resulting in a greatly enhanced polishing rate. A model based on the Valence Alternation Pairs was proposed to explain this selective corrosion behavior of Te element in the amorphous GST. Acknowledgement \* This work was financially supported by the Acceleration Research Program of the Korea Science and Engineering Foundation and the Brain Korea 21 Project in 2009. We thank SUMCO Corp. and Hynix Semiconductor Inc. for helping us with our experiments.



## SESSION II4: Mechanochemistry in Tribology and Milling

Chair: Matthias Scherge

Tuesday Morning, December 1, 2009

Room 108 (Hynes)

**8:30 AM II4.1****Mechanochemistry of Carbon Tribo Materials.** Michael Moseler, Tribosimulation and Multiscale Modelling, Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany; Physics Department, University of Freiburg, Freiburg, Germany.

Carbon is an ubiquitous element in technical tribology occurring e.g. in lubricants, tribological coatings and tribo-mutation layers. Despite the fact that diamond and diamond-like carbon coatings (DLC) [1] are used in an increasing number of applications, not much is known about the atomic scale processes that occur during sliding these films. For instance, the mechanical and chemical processes that occur during the running-in of DLC films [2] or the polishing of diamond are still poorly understood [3]. Molecular dynamics is ideally suited to gain a deeper understanding of the underlying processes. Here simulations with a novel Brenner bond order potential [4] are reported. The running-in of hydrogenated DLC is explained by a combination of smoothing and chemical passivation of a DLC/DLC interface. Fluctuations in the friction coefficient of the DLC coatings can be explained by welding of the DLC/DLC tribosurfaces, combined with the formation of a transfer film (transferred from one DLC partner to the other) and the establishment of a new tribointerface with low friction coefficient. For diamond polishing, the occurrence of soft polishing direction can be related to the generation of thick amorphous layers that are not stable with respect to oxidation or mechanical wear. The wear rate (i.e. the velocity of the diamond/amorphous-carbon interface) depends crucially on the diamond surface orientation with the highest speed found for (110) surfaces that are rubbed in the (001) direction, while the lowest interface speed was observed for the diamond (111) surface. These findings are in perfect agreement with a 600 years old experimental knowledge of diamond polishers. The observed anisotropy of the wear rates is rationalized within a simple model that describes the amorphisation process as a mechanically guided chemical reaction. [1] M. Moseler, P. Gumbsch, C. Casiraghi, A. Ferrari, J. Robertson, The ultrasoothness of diamond-like carbon surfaces, *Science* 309, 1545 (2005) [2] L. Pastewka, S. Moser, M. Moseler, B. Blug, S. Meier, T. Hollstein, P. Gumbsch, The running-in of amorphous hydrocarbon tribocoatings: a comparison between experiment and molecular dynamics simulations, *Int. J. Mat. Res.*, 10, 1136 (2008) [3] J. Hird and J. Fields, Diamond polishing, *Proc. R. Soc. Lond.* 460, 3547 (2004) [4] L. Pastewka, P. Pou, R. Perez, P. Gumbsch, M. Moseler, Describing bond-breaking processes by reactive potentials: the importance of an environment-dependent interaction range, *Phys. Rev. B* (R) 78, 161402 (2008)

**9:00 AM II4.2****Modelling of the Tribochemistry of  $H_2O$ ,  $w>2$  and  $H_2O$  Gases on Diamond Surfaces.** Haibo Guo<sup>2</sup> and Yue Qi<sup>1</sup>; <sup>1</sup>Materials and Processes Lab, GM R&D Center, Warren, Michigan; <sup>2</sup>Mechanical Eng., University of South Carolina, Columbia, South Carolina.

The friction of both diamond and diamond-like carbon (DLC) coatings can be dramatically changed by active gases in the environment, such as hydrogen, oxygen, and water vapor, due to tribochemical reactions. To understand the atmospheric effects and to predict the optimized environmental conditions (gas species, pressure and temperature), the tribochemical reactions on diamond surfaces are modeled from first principles thermodynamics. The results show that: both  $H_2$  and the mixture of  $H_2O$  plus  $O_2$  (such as humid air) can effectively achieve low friction with a fully -H or -OH passivated surface at very low partial pressures. Water vapor itself can passivate diamond (111) and (100) surfaces into half -H and half -OH terminated surfaces, but only at unrealistically high partial pressures, thus water vapor alone can't effectively achieve low friction on diamond surfaces. However, the -O terminated diamond surface could lead to desorption of CO and/or  $CO_2$ , causing gradual wear and structural degradation of carbon films, and leaving dangling bonds which lead to high frictions. Thus oxygen is not suitable for a friction-resistant passivation. In all tribochemical reactions considered, the partial pressure required to reach low friction increases rapidly with temperature; and diamond (100) surface requires less partial pressures than (111) surface.

**9:15 AM II4.3****Nanomaterials Synthesis Using Mechanochemistry.** Ying Chen, Institute for Technology Research and Innovation, Deakin University, Geelong, Victoria, Australia.

Many chemical reactions which take place often at very high-temperatures can be realised by mechanical actions (milling and grinding) even at room temperature. Because of the low temperature, the reactions initiated by external mechanical force cannot progress continuously. Therefore, the end-products of the cold mechanochemical reactions are often at nanometer scale. This presentation reports the formation of various nanostructures including nanotubes, nanowires, nanospheres, and nanocrystals via mechanochemistry route.

**9:30 AM II4.4****Mechanochemical Synthesis of Novel Sensor Materials.** Monica Sorescu<sup>1</sup>, Lucian Diamandescu<sup>2</sup> and Adelina Tomescu<sup>2</sup>; <sup>1</sup>Duquesne University, Pittsburgh, Pennsylvania; <sup>2</sup>National Institute for Materials Physics, Bucharest, Romania.

Zinc and zirconium-doped hematite nanoparticles of the type  $xZnO-(1-x)\alpha-Fe_2O_3$  and  $xZrO_2-(1-x)\alpha-Fe_2O_3$  ( $x=0-1$ ) were obtained using mechanochemical activation and characterized by X-ray diffraction (XRD), Mossbauer spectroscopy and



conductivity measurements. XRD patterns yielded the dependence of lattice parameters and particle size as a function of ball milling time for each value of the molar concentration  $x$ . The particle dimension reached the value of 9 nm after 24 hours of ball milling. The  $x=0.1$  spectra are consistent with line broadening as Zn substitutes Fe in the hematite structure and the appearance of the zinc ferrite phase at milling times longer than 4 hours. For  $x=0.5$  the zinc ferrite phase occurred at 2 hours and entirely dominated the spectrum at 24 hours milling time. The quadrupole split doublet, with the hyperfine parameters characteristic to  $\text{ZnFe}_2\text{O}_4$ , was observed in the Mossbauer spectrum for  $x=0.5$  and 24 hours of milling, demonstrating that the entire system of nanoparticles consists finally of zinc ferrite. As  $\text{ZnO}$  is not soluble in hematite in bulk form, the present study clearly demonstrates that the solubility limits of an immiscible system can be extended beyond the limits in the solid state by mechanochemical activation. For the zirconium-doped hematite system, the Mossbauer spectra were fitted with one or alternatively, four sextets, corresponding to Zr ions substituting Fe ions in the hematite structure and further required the addition of a quadrupole split doublet, representing Fe substituting Zr in the  $\text{ZrO}_2$  lattice. This compositional transition can be in principle evidenced by recording the recoilless fraction ( $f$ ) as a function of the ball milling time, provided there is a precise enough method to do so. We applied the dual absorber method developed by us for the precise determination of the recoilless fraction using a second absorber (a stainless steel foil) and a single room temperature Mossbauer spectroscopy measurement. Indeed, we observed the occurrence of a minimum in the values of the recoilless fraction for each molarity, followed by a further decrease of the  $f$  factor due to the appearance of nanoparticles in the system. We further correlated the structural properties of the zirconium-doped hematite system with the sensing properties. These were measured as a function of temperature, gas concentration (carbon monoxide and methane) and variable humidity of air. The material system was found to be sensitive over the entire range of CO concentrations and the linearity of the sensor signal was not affected by the relative humidity of air, which makes it the ideal system for sensing devices.

#### 9:45 AM II4.5

**Tension-Induced Radical Generation in Polymers Without Chain Scission.** Jeremy M. Lenhardt, Robert Choe and Stephen L. Craig; Department of Chemistry, Duke University, Durham, North Carolina.

The incorporation of appropriately substituted, strained cyclopropanes along the main chain of a polymer provides a mechanism for mechanically-induced homolytic carbon-carbon bond scission along the polymer main chain. Thousands of radicals can be generated under elongational shear conditions in which only a single polymer scission event is observed. The generated radicals thus generated are reactive and can trap nitroxides from surrounding solution. Counterintuitively, the selectivity rules governing the stress-induced diradical generation and stress-free recombination reactions are such that net isomerization reactions along the polymer main chain can be driven far from equilibrium, and intermittent tension on the polymer is shown to result in a net contraction of effective polymer contour length, irrespective of molecular weight degradation.

#### SESSION II5: Mechanochemistry in Tribology

Chair: Michael Moseler

Tuesday Morning, December 1, 2009

Room 108 (Hynes)

#### 10:30 AM II5.1

**Accelerated Molecular Dynamics Simulations of Atomic-Scale Friction on Amorphous Silica Surfaces: Temperature and Sliding Velocity Dependence.** Woo Kyun Kim<sup>1</sup> and Michael L. Falk<sup>1,2,3</sup>; <sup>1</sup>Materials Science and Engineering, The Johns Hopkins University, Baltimore, Maryland; <sup>2</sup>Mechanical Engineering, The Johns Hopkins University, Baltimore, Maryland; <sup>3</sup>Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland.

Accelerated molecular dynamics (MD) is applied to investigate the temperature and sliding velocity dependence of friction between two oxidized silicon crystals. While the smallest sliding velocity reachable by conventional MD technique is on the order of 1.0 meter per second, several orders of magnitude faster than experiments, our new methodology makes it possible to reduce sliding velocity up to four orders of magnitude closer to the regime of the actual experiments. This scheme is a parallelized version of Voter's hyperdynamics with a more computationally efficient biased potential. Accelerated simulations model recent Atomic Force Microscope (AFM) experiments that observed friction force becoming less dependent of sliding velocity as temperature rises, an effect not predicted by the Tomlinson model. Simulation results show these deviations come from the existence of multiple transition mechanisms. While only the most probable mode dominates transitions at lower temperatures, multiple mechanisms compete with each other as temperature increases. During the sliding simulations at various temperatures and sliding velocities, the dependence of friction force on the normal force is also explored. Moreover, the effects of surface termination and chemistry, especially the ratio of the number of non-bridging oxygen (NBO) atoms to the number of bridging oxygen atoms, on sliding are studied.

#### 10:45 AM II5.2

**Friction as a Function of Temperature Investigated with Thermal AFM Probes.** Christian Greiner<sup>1</sup>, Jonathan Felts<sup>2</sup>, Zhenting Dai<sup>2</sup>, William P. King<sup>2</sup> and Robert W. Carpick<sup>1</sup>; <sup>1</sup>Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>2</sup>Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Champaign, Illinois.

The physical mechanisms behind the energy dissipation in frictional solid-solid contacts are still not fully understood. This understanding is essential to model and predict tribological systems as well as to develop materials with tailored frictional behavior. Atomic force microscopy (AFM) is a very powerful tool to investigate tribological contacts in a fundamental way,



because with AFM it is possible to reduce the solid-solid contact problem to that of a single asperity. Recently, a few research groups have employed AFM to investigate single asperity friction as a function of temperature. Almost all of these studies were carried out under cryogenic conditions and investigations above room temperature are lacking. As well, all published studies have involved heating the sample, and not the tip. A heated tip provides an alternate means to vary the temperature of the contact and is potentially more representative of the localized heating that can occur in a real tribological interface. Here, we used custom AFM probes with integrated solid-state heaters which allowed for the tip temperature to be controlled between room temperature and 800°C. With these probes we systematically investigated the nanotribological behavior of single asperity contacts between the silicon tip and a silicon sample (both with a native oxide). According to preliminary results, we observe a strong dependence whereby friction increases significantly with temperature. This is in contrast to cryogenic measurements which show the opposite trend. The behavior is reversible, indicating that the effects are not due to damage or modification of the tip or sample. We will discuss how the results of this study enable us to examine the underlying energy loss mechanisms and their activation energies.

#### 11:00 AM II.5.3

**Force-Controlled Molecular Conductivity.** Ke Wang, Norma Rangel, Subrata Kundu, Roberto Tovar, Jorge Seminario and Hong Liang; Mechanical Engineering, Texas A&M University, College Station, Texas.

A mechanical force has significant advantages in controllability on any materials it is loaded on. Here we discuss about the controllability of molecular conductivities of a citrate. Approaches were made in experimental study and molecular simulation of a citrate capped on and linked between gold nanoparticles (AuNPs). We found that the molecular conductivity depends on the pathways of electrons that were controlled by the applied mechanical stress. Under stress, we could turn the conductivity up and down for about ten-fold.

#### 11:15 AM II.5.4

**Tribochemistry in Engines: The Role of Soot.** Matthias Scherge<sup>1,2</sup>, Martin Dienwiebel<sup>1</sup> and Steffen Antusch<sup>3</sup>; <sup>1</sup>Mikrotribologie, Fraunhofer IWM, Karlsruhe, Germany; <sup>2</sup>Technische Physik I, Technische Universität Ilmenau, Ilmenau, Germany; <sup>3</sup>Material- und Prozessentwicklung, Forschungszentrum Karlsruhe, IMF III, Karlsruhe, Germany.

The influence of the most prominent types of combustion soot on the mechano-chemistry in internal combustion engines was investigated. The sooted oils were generated by dynamometer tests using modern engines with different combustion technologies. Mechano-chemistry was studied using a combination of pin-on-disk tribometer coupled to a high resolution wear measurement system (RNT) and high resolution physico-chemical analysis. The soot particles were analyzed by transmission electron microscopy (TEM), energy electron loss spectroscopy (EELS), x-ray photoelectron spectroscopy (XPS) and electron spin resonance (ESR). By comparison with Carbon black and diamond we can conclude that the wear property does not depend on the mechanical properties of different soot particles but is closely related to their reactivity and the amount of defect sites.

#### 11:30 AM II.5.5

**On-line Topographical Investigation of Lubricated Sliding Copper Surfaces with a Novel Tribometer.** Spyridon Korres<sup>1,2</sup>, Matthias Scherge<sup>2,1</sup> and Martin Dienwiebel<sup>1,2</sup>; <sup>1</sup>Institute for Reliability of Components and Systems, University of Karlsruhe, Karlsruhe, Baden Wuerttemberg, Germany; <sup>2</sup>Tribology, Fraunhofer Institute for Mechanics of Materials, Freiburg, Baden Wuerttemberg, Germany.

We present the first results of the tribological investigation of lubricated copper surfaces against steel. Parallel measurements of friction and surface topography give an insight in the dynamic processes that occur on the copper surface. Several tests were conducted on dry, as well as lubricated samples with optically transparent poly-alpha-olefin. The experiments were conducted with a novel experimental platform that links topographical and material changes with the friction and wear behavior of oil-lubricated metal surfaces. This tribometer combines state of the art methods for the analysis of the surface topography on the micro and nano-scale and on-line wear measurement. Information of the topography of one of the two surfaces is gathered *in-situ* with a holography microscope. Sub-micrometer lateral resolution images are acquired with an atomic force microscope (AFM). A radio nuclide technique (RNT) unit allows for on-line wear monitoring.

#### 11:45 AM II.5.6

**Electrochemical Growth Model and Wear of Properties of Eco-friendly Trivalent Chromium Layers.** Jong J. Lee<sup>1</sup>, Yong Choi<sup>1</sup> and Sang H. Lee<sup>2</sup>; <sup>1</sup>Advanced Materials Engineering, Sunmoon University, Asan, Korea, South; <sup>2</sup>Electronic Engineering, Sunmoon University, Asan, Korea, South.

Eco-friendly trivalent chromium layers were prepared in modified chromium sulfate and chromium chloride baths by pulse plating with ultrasonic agitation to replace hexavalent hard chromium coating in industrial fields. Deposition rate of the trivalent chromium layers by ultrasonic pulse plating were lower than that by direct current plating at a same total on-time. Wear resistance of the trivalent chromium layers prepared by ultrasonic pulse plating was higher than that of the chromium layer prepared by direct current plating. The ultrasonic agitation during pulse plating resulted in increasing neutral salt fog spray life and wear resistance, which are related to the microstructure of the layers in which smaller crack size and more broad size distribution of the trivalent chromium layers existed. Nucleation and growth models of electroplated chromium layers under the pulse plating was proposed to explain microstructure development related to the wear behavior based on electrochemical equation and microstructure observation by field ion electron microscopy and transmission electron microscopy, respectively.



SESSION II6: Mechanochemistry under Extreme Conditions  
 Chair: Matthias Scherge  
 Tuesday Afternoon, December 1, 2009  
 Room 108 (Hynes)

**1:30 PM II6.1**

**Experimental and Quantum Molecular Dynamics Studies of Shock-Induced Chemistry in Simple Hydrocarbons.** Marc Cawkwell<sup>1</sup>, Edward Sanville<sup>1</sup>, Nicolas Bock<sup>1</sup>, Matt Challacombe<sup>1</sup>, Anders Niklasson<sup>1</sup>, Thomas D. Sewell<sup>2</sup>, Dana Dattelbaum<sup>3</sup> and Stephen Sheffield<sup>3</sup>; <sup>1</sup>Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico; <sup>2</sup>Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri; <sup>3</sup>Dynamic and Energetic Materials Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

The decomposition or polymerization of molecules under shock compression is a classical example of mechanochemistry. We have performed a series of experiments on simple hydrocarbons in order to quantitatively define structure-property relationships for reacting materials under shock compression. Embedded gauge experiments on tert-butylacetylene, 1,3- and 1,4-cyclohexadiene, and benzene in a two-stage light gas gun provide convincing evidence for volume changes that are consistent with polymerization and/or decomposition. However, experiment alone cannot unambiguously identify these reactions or the specific sequence of bond making and breaking events. We have recently developed a parallel, linear scaling quantum molecular dynamics simulation package that is based on the self-consistent charge transfer tight-binding approximation. Our interatomic potential for hydrocarbons provides an accurate and transferable representation of the bonding, structure, and reactivity of organic molecules. Long-duration simulations of the hydrocarbons studied experimentally have been performed under Hugoniot conditions. These simulations have enabled us to associate features in the measured wave profiles to specific chemical events. Thus, we will describe a synergistic set of simulations and experiments that clarify some aspects of mechanically induced chemistry in reactive organic liquids.

**1:45 PM II6.2**

**Determination of Milling Parameters to Obtain Magnetite Nanoparticles from Iron Metal by Wet-Milling.** Musa M. Can, Sadan Ozcan, Abdullah Ceylan and Tezer Firat; Physics Engineering, Hacettepe University, Ankara, Turkey.

Soft magnetic nanoparticles systems have been of long standing interest due to their fundamental scientific interest and also for their vast technological applications. Especially Fe<sub>3</sub>O<sub>4</sub> nanoparticles, have been of major interest to many researchers because of being efficient ferrofluids, having magneto resistance, performing strong magnetic property, and generating low toxicity in biological and medical applications. In this study nanosize magnetite (Fe<sub>3</sub>O<sub>4</sub>) particles have been prepared directly from metallic iron (Fe) powder within distilled water (H<sub>2</sub>O) by using a planetary ball-mill. Amongst the milling parameters, our attention has been on the effects of milling time on the formation of magnetite. According to XRD analyses, the amount of Fe decreases and is being transformed into Fe<sub>3</sub>O<sub>4</sub> with the increasing milling time. As it is known very well, there are two phases of Fe called as magnetite and maghemite. These two phases demonstrate very similar diffraction patterns. Therefore, we further analyze the samples by FTIR spectroscopy to verify the structure as well as employing chemical analysis methods. FTIR spectra have clearly revealed absorption peaks around 628, 581 and 443cm<sup>-1</sup> which are in good agreement with the characteristic absorption peaks of Fe<sub>3</sub>O<sub>4</sub>. Chemical analyses have shown that the total composition of Fe in the samples is 73.04% which contains 24.10% Fe<sup>2+</sup> and 49.34% Fe<sup>3+</sup>. This result is in accordance with the theoretically estimated values. To the best of our knowledge this study is the first to show the synthesis of pure Fe<sub>3</sub>O<sub>4</sub> nanocrystalline powder in a single step process based on reactive milling of metallic Fe.

**2:00 PM II6.3**

**Collision Synthesis of Unique Carbon Nanomaterials Inspired by the Allende Meteorite.** Satoshi Ohara, Zhenquan Tan, Kazuyoshi Sato and Hiroya Abe; Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka, Japan.

A simple shock event approach inspired by the Allende meteorite to produce sophisticated carbon nanomaterials is reported. It is demonstrated that unique carbon nanostructures, including carbon nanotubes, carbon onions, and new carbon nanorings are synthesized by high-speed ball-milling of steel balls. The carbon nanorings have diameter of several ten nanometers. It is considered that the gas-phase reaction takes place around the surface of steel balls under local high temperatures induced by the collision energy in ball-milling process, which results in phase separated unique carbon nanomaterials.

**2:15 PM II6.4**

**Laser Shock Compression and Spalling of Reactive Ni-Al Laminate Composites.** Chung-Ting Wei<sup>1</sup>, Brian Maddox<sup>3</sup>, Timothy P. Weihs<sup>2</sup>, Adam K. Stover<sup>2</sup>, Vitali F. Nesterenko<sup>1</sup> and Marc A. Meyers<sup>1</sup>; <sup>1</sup>Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, California; <sup>2</sup>Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; <sup>3</sup>Lawrence Livermore National Laboratory, Livermore, California.

Reactive laminates produced by successive rolling and consisting of alternate layers of Ni and Al (with bi-layer thicknesses of 5 and 30  $\mu$ m) were investigated by subjecting them to laser shock-wave loading. The laser intensity was varied between  $\sim 2.68 \times 10^{11}$  W/cm<sup>2</sup> (providing an initial estimated pressure  $P \sim 25.6$  GPa) and  $\sim 1.28 \times 10^{13}$  W/cm<sup>2</sup> ( $P \sim 337.1$  GPa) with two distinct initial pulse durations: 3 ns and 8 ns. Hydrodynamic calculations (using commercial code HYADES) were conducted to simulate the behavior of shock-wave propagation in the laminate structures. SEM, EDS, and XRD were carried out on the



samples to study the damage, failure modes, reaction initiation, and spall due to the laser-surface interaction. It was found that the thinner bilayer thickness (5  $\mu\text{m}$ ) laminate exhibited localized interfacial reaction at the higher laser intensity ( $1.28 \times 10^{13} \text{W/cm}^2$ ); the reaction products were identified as NiAl and other Al-rich intermetallic compounds. The reaction front and the formation of intermetallic compounds extend into the sample with a thinner bilayer thickness (5  $\mu\text{m}$ ) to a depth of about 50  $\mu\text{m}$ . Based on microstructural observations the estimated highest temperature in the experiments is about 1470K, and cooling rate of reaction products was  $5.7 \times 10^5 \text{K/s}$  and cooling time 2.1ms approximately. Increase in the duration of laser shock wave induces increased reaction, which occurs also in the thicker bilayer laminate samples (30  $\mu\text{m}$  bi-layer thickness). It is demonstrated that the methodology of laser shock is well suited to investigate the threshold conditions for dynamic mechanical reaction initiation caused by high intensity laser.

#### 2:30 PM II6.5

**Optimization of Planetary Ball-milling Conditions for Synthesizing SiC.** Yasuhiro Kodera<sup>1</sup>, Kazuki Saeki<sup>1</sup>, Naoki Toyofuku<sup>1</sup>, Manshi Ohyanagi<sup>1</sup> and Zuhair A. Munir<sup>2</sup>; <sup>1</sup>Ryukoku University, Otsu,, Shiga, Japan; <sup>2</sup>Chemical Engineering and Materials Science, University of California, Davis, Davis, California.

Synthesizing SiC powder through mechanical alloying (MA) is considered as an effective method to achieve full consolidation of SiC without a sintering additive. The complete reaction of Si-C required a long milling time, such as 24h, which might be shortened by the optimization of milling operative conditions. We present the results of an investigation into the influence of milling operative conditions (the revolution speed of the disk (Wp), the rotation-to-revolution speed ratio in planetary ball milling (Wv/Wp), the ball filling fraction in vial (BFF) and so on) on synthesizing SiC in planetary ball mill. There is the equation which is able to estimate the total power (P) transferred from the mill to the system in various operative conditions. This equation suggested that the increase of Wp and Wv/Wp, and the decrease of BFF play an important role in improving milling performance and shortening MA time. When Wp increased from 300 to 400 rpm, the MA time completing Si-C formation was reduced from 24 to 5 h. The milling performance was increased by changing Wv/Wp ratio from -1 to -1.6, and rapidly decreased after Wv/Wp reached over -2.0, as a result of ball motion change. The 15% BFF leaded highest milling performance while Wp and Wv/Wp were 400rpm and -1.18, respectively. Also, the relationship between P and the electrical power consumption during the milling process was discussed. The most suitable milling conditions, which are obtained in this study, significantly shorten MA time from 24 to 2 h.

#### 2:45 PM II6.6

**Sonochemistry-Induced Fast Formation of Large Single Crystals of Mercury-mercaptide Directly From Liquid Mercury.** Boaz Pokroy<sup>1,2</sup>, Barbara Aichmayer<sup>3</sup>, Anna Schenk<sup>3</sup>, Sung Hoon Kang<sup>1</sup>, Fratzl Peter<sup>3</sup> and Joanna Aizenberg<sup>1</sup>; <sup>1</sup>Harvard University, Cambridge, Massachusetts; <sup>2</sup>Materials Engineering, Technion - Israel Institute of Technology, Haifa, Israel; <sup>3</sup>Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.

The synthetic formation of metal-mercaptide compounds has now been known for almost 200 years. These compounds are usually formed by the reaction of mercury salts (some examples are: mercury - nitrate, iodide, chloride or cyanide) with thiolates or disulfides to produce  $\text{Hg}(\text{S-R})_2$  followed by crystallization of the latter from ethanol. In this work we will show that by sonicating a mixture of liquid metal mercury and a neat alkanethiol solution using medium-intensity ultrasound, one can synthesize large crystals of mercury mercaptide within seconds, which have the same crystallographic structure as crystals grown for several days by the conventional method. We will present high-resolution imaging as well as synchrotron WAX/SAXS and micro-beam diffraction data of the mercury-mercaptide crystals grown by our method. These results demonstrate for the first time that sonochemical approach enables extremely fast production of crystals directly from liquid mercury and that the quality, size and shape of these crystals are superior to those produced from mercury salts by conventional crystallization. We will discuss the mechanism of crystal growth via self-assembly.



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